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An artificial panel produced by sorting residue of copper clad laminate

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Abstract

Copper Clad Laminate (CCL) are used in printed circuit boards (PCBs) as base material. When PCBs are wasted, a large amount of sorting residue are disposed badly in China, mainly by stacking in the field, which may cause secondary pollution and resource-wasting. In this study, a type of artificial panel (AP) has been produced by the sorting residue of CCL (SRCCL). The AP is produced by a self-developed mechanical former through adding resin paste as a bonding agent. Furthermore, micro-shapes of SRCCL and effects of the contents on mechanical properties of the AP are investigated. It has been found that SRCCLs are in the form of fiber bundles, with the majority of fibers being encapsulated in resin. When SRCCL content was 70 wt %, the AP has excellent mechanical properties, which results in a flexural strength of 25.85 MPa. This technique offers a possibility for recycling of SRCCL and resolving the environmental pollutions during recycling of PCBs.

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Keywords: sorting residue of copper clad laminate, artificial panel, resin, mechanical properties

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1. Introduction

1.1 The production of SRCCL

The production of Electrical and Electronic Equipment (EEE) is one of the fastest growing sectors of manufacturing industry in the world. Murugan¹ pointed out that the generation rate of Waste Electrical and Electronic Equipment (WEEE) is high worldwide and continues to increase, being one of the fastest and most growing waste flows.

The printed circuit board (PCB) production in mainland China have accounted for 42.59% of global production in 2013². A big waste is generating nowadays due to the growing demand for innovation and the fact that more and more products have a reduced life expectancy³.

Copper Clad Laminate (CCL) is the key raw material to produce PCBs. The waste CCL is produced during the cutting procedure. In recent years, the production of the CCL in China ranks first steadily in the world. The CCL production had reached 482.31 million m² and the waste CCL has even reached 106.10 million m² in 2013⁴.

Waste CCL was preliminary broken into smaller pieces and then was pulverized. Cu powder was separated through gravity separation and hydraulic shaker. After multi stage precipitation for recycling, the sorting residue was reserved and dried in open air.

The typical composition of SRCCL is thermosetting resins (epoxy), glass fiber, plastic, reinforcement materials, additives and other brominated flame retardants (BFRs) and represents about 70 wt % of PCBs. The material compositions vary according to sources and type of PCBs and waste separation process⁵. Iji and Yokoyama⁶ found that the non-metallic fractions consisted of glass fiber (65 wt %), cured epoxy resin (32 wt %), and impurities (copper: < 3 wt %, soldering alloys: < 0.1 wt %).

1.2 The review of the sorting residue of CCL (SRCCL) recycling

In general, the methods of recycling SRCCL are basically composed of physical recycling methods and chemical recycling methods⁷. The chemical recycling methods include pyrolysis, gasification and incineration, etc. The physical recycling methods include reinforcing filler for thermoplastic resins, production of phenolic molding composites, composite boards, building materials modeling material, specific products such as sewer grates and surfboat in amusement park, etc⁸⁻¹³. The recycling of SRCCL is much more difficult than the routine waste recycling because the compositions of the SRCCL are diverse, complex and even toxic. The fundamental issue in the physical recycling of SRCCL is how to use it in an effective, cheap and safe way¹⁴.

1.3 The disposition status of SRCCL

It is officially reported that SRCCLs are disposed of by incineration or landfill. But it is found that large quantities of residue are stacking in the field without being properly treated, which occupy plenty of land. Moreover, stacking in the field will also lead to secondary pollution caused by heavy metals and BFRs.

Sepúlveda¹⁵ reported that abundant toxic materials including heavy metals and BFRs can easily be found in used PCBs. BFRs are commonly used in electronic products to meet fire regulations. The widespread production and use of BFRs increase contamination of the environment, wildlife, and people¹⁶. In addition to BFRs, metal is also an important hazardous substance that is released from e-waste recycling¹⁷. With great potential to accumulate in vital organs of the human body, heavy metal can do harm to human health causing mutagenesis carcinogenesis and teratogenesis.

1.4 The study content in this paper

Firstly the characteristics and the composition of SRCCL were analyzed using a scanning electron microscope and GC-MS. In order to take full advantage of SRCCL, a novel technique has been developed to make a type of artificial panel (AP) constituted of the SRCCL and adhesive. Furthermore, the micro-shapes of SRCCL and effects of surface modification on mechanical properties of the AP are investigated, including its infrared spectrum, flexural strength, density and water absorption. The aim of this research is to develop a new technique for recycling non-metallic materials and resolving the environmental pollution during recycling of PCBs.

2. Materials

The unsaturated polyester resin used in the study was CS388-1 Lotus brand. The curing agent was the methyl ethyl ketone peroxide and the accelerator was the cobalt isooctanoate. The SRCCLs were sampled from the Sha Xi Waste Copper Clad Laminate Residue Yard in Qingyuan, Guangdong. Styrene AR was purchased from Yong Da Chemical Reagents Development Center in Tianjin. The coupling agent KH570 was purchased from Dongguan Shan Yi Plasticizing Co., LTD.

3. Methods

3.1 Preparation of AP

Firstly 1% coupling agent and 1% styrene (relative to the SRCCL, wt %) were well-mixed as a modification agent, which was sprayed on the surface of the SRCCL and then stirred uniformly in a material barrel. After drying at 100°C, the surface modification for SRCCL was finished. A mixture of adhesive made by the unsaturated polyester resin, curing agent and accelerator was prepared under certain ratio. Mix the adhesive and the SRCCL uniformly to achieve a prototype. Then the prototype was transferred into a mold. After vacuum pumping, the prototype was treated under a certain pressure (0.6 MPa) and frequency (vibration force: 12 KN) for 3 min. Afterwards the AP was removed from the mold and transferred into an oven at 90°C for 4h. Finally the AP was grinded and polished. The producing process of the AP is shown in fig.1.

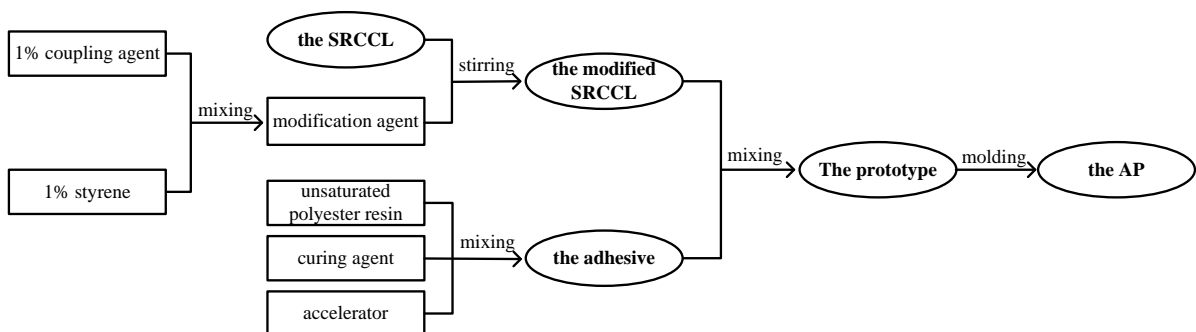


Fig. 1. Flowchart of preparation of AP

3.2 Properties test

Microscopic observation and analysis. The scanning electron microscope Quanta 200 purchased from the Holland FEI Company was used to observe and analyze the micro-shapes of the SRCCL particles as well as the AP.

Infrared spectrum analysis. The Fourier transform infrared spectrometer VERTEX 33 purchased from the Bruker Company (Germany) was used to analyze the SRCCL particles after modification.

Flexural strength. Flexural strength was determined in accordance with GB/T 11718-2009 using an electronic universal testing machine.

Density test. Density was determined in accordance with GB/T 17657.

Water absorption test. Water absorption was determined in accordance with GB/T 17657.

4. Results and discussion

4.1 SRCCL composition analysis

The composition of the SRCCL stacked in the wild was analyzed. The analysis was carried out after drying, therefore the moisture content was not included.

Table 1. The composition analysis of the SRCCL

Serial number	The name of the compound	Quality percentage (%)	Effect
1	Bisphenol A epoxy resin	~28-29	resin
2	brominated epoxy resin	~11-12	resin
3	Glass Fiber	~44-45	reinforcing filler
4	Mineral Wool	~12-13	reinforcing filler
5	magnesium hydroxide (Mg(OH) ₂)	~0.2-0.3	Flame retardant
6	Copper (Cu)	~1.3-1.4	/
7	Iron (Fe)	~0.02-0.03	/
8	Nickel (Ni)	~0.004	/
9	Titanium (Ti)	~0.15-0.16	/
10	Zinc (Zn)	~0.016	/
11	Strontium (Sr)	~0.007	/
12	Barium Sulfate (BaSO ₄)	~0.1-0.2	/
13	Zirconia (ZrO ₂)	~0.05	/
14	Silane coupling agent	~0.3-0.5	Coupling agent

As table 1 indicates the content of resin (39% ~ 41%), glass fiber and mineral wool (56%~58%). These three substances accounts for 95-99% of the residue and the rest of the 1-5% are coupling agent, flame retardant and heavy metal. The result is similar to the study of Iji and Yokoyoma, indicating content of resin (32 wt %), glass fiber (65 wt %) and impurities (copper: < 3 wt %, soldering alloys: < 0.1 wt %)⁵.

4.2 SRCCL micro-shape analysis

The scanning electron microscope (SEM) was applied to compare and analyze the micro-shape of SRCCL. Fig. 2. (a-d) shows the microstructure of the SRCCL from 10μm to 100μm.

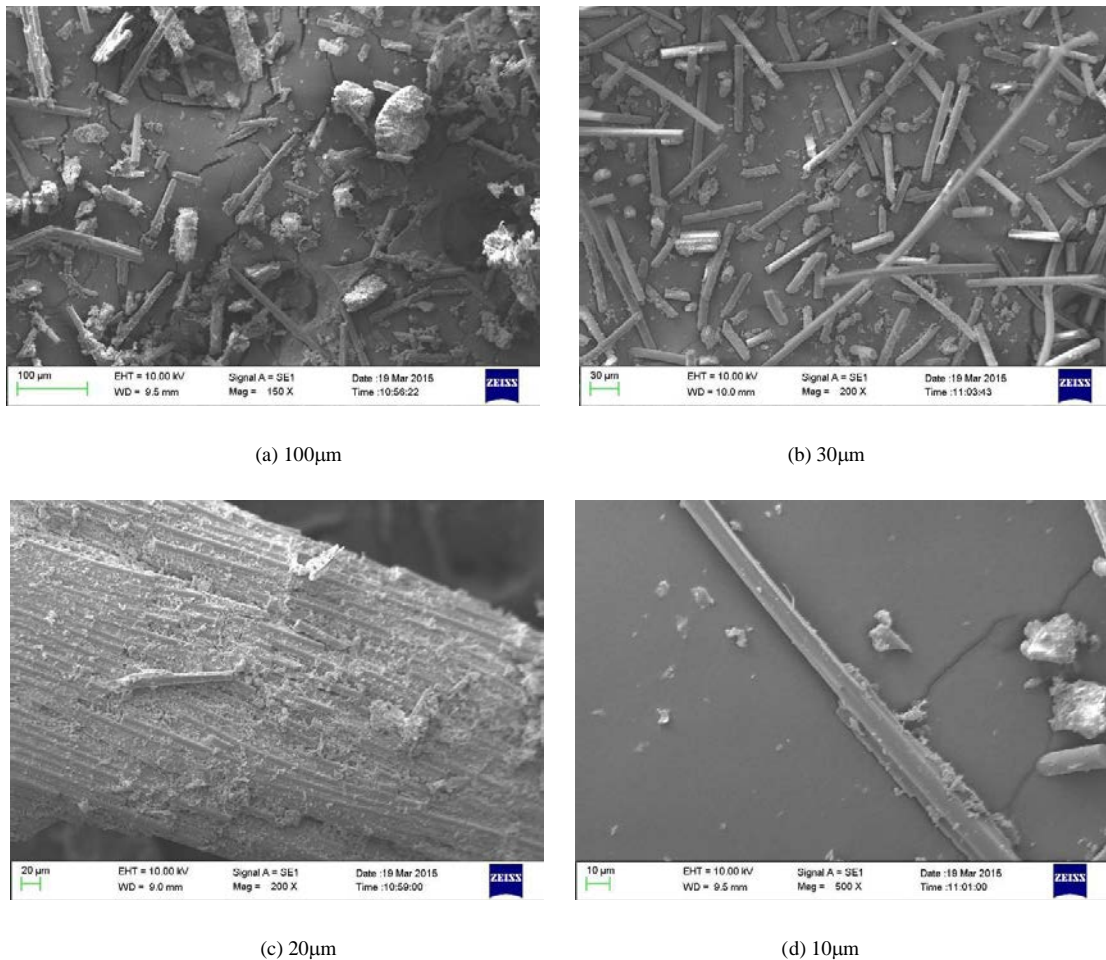


Fig. 2. SEM photographs of microstructure of SRCCL (a) 100μm SRCCL (b) 30μm SRCCL (c) 20μm SRCCL (d) 10μm SRCCL

According to Fig. 2. (a) and (b), the SRCCL have a large number of glass fiber with relatively complete surface with the size ranging from 20μm to 100μm. Besides, agglomerates are observed in the SRCCL. Therefore, agglomerates are zoomed in (c) and (d). Fig. 2. (c) indicates that the agglomerates are glass fiber not being completely shattered. In another word, some small size glass fiber is surrounded by resin. Fig. 2. (d) shows that the glass fiber is not complete and with resin on the surface in the perspective of 10μm.

4.3 Content of AP

The effect of amount of SRCCL was investigated. The SRCCL was added to the adhesive, comprising of polyester resin (99.25%), accelerant (0.5%) and curing agent (0.25%), at proportions of 70%. The results are shown in table 2.

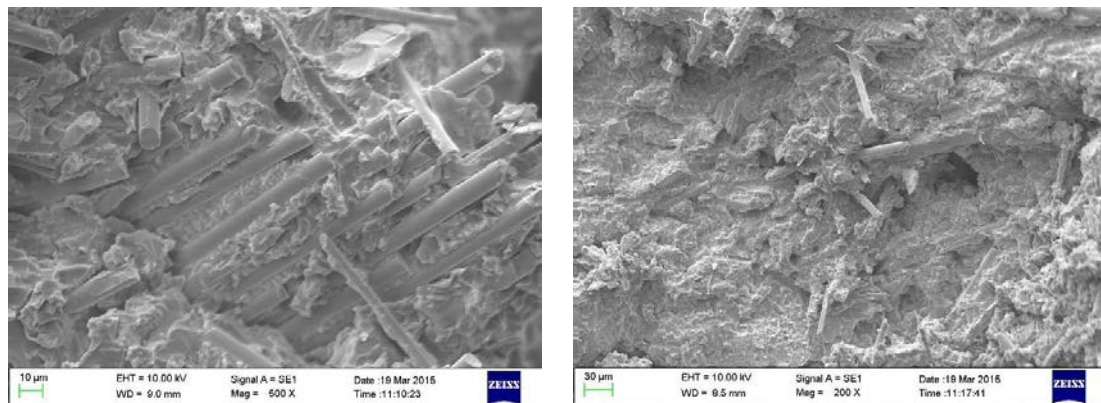
Table 2. Physical properties of the AP

Number	SRCCL (%)	Adhesive (%)	Surface modification agent (%)	Density (g/cm ³)	Water absorption (%)	Flexure strength (MPa)	
						Before soaking	After 12-hour soaking
1# unmodified	70	30	0	1.46	0.8	9.72	9.58
2# modified	70	30	2	1.71	0.3	25.85	25.67

As the results of sample 1# & 2# shows the AP prepared by 70% modified SRCCL not only reduces the dosage of the adhesive, but also manifests a better physical properties than unmodified one. The flexure strength is over 25MP before and after soaking, being 74.88% higher than the unmodified. The water absorption is 0.3% being 50% lower than the unmodified one, with a higher density of 1.71 g/cm³.

4.4 Effect of surface modification

The SEM was used to investigate the morphology of the AP with and without modification.



(a) Unmodified

(b) Modified

Fig. 3. (a) SEM photo of AP made by unmodified SRCCL (b) SEM photo of AP made by modified SRCCL.

As shown in fig. 3. (a) and (b), the density of the AP made by modified SRCCL is higher than the unmodified one. And the AP after modification can obtain a better combination of the glass fiber and the adhesive.

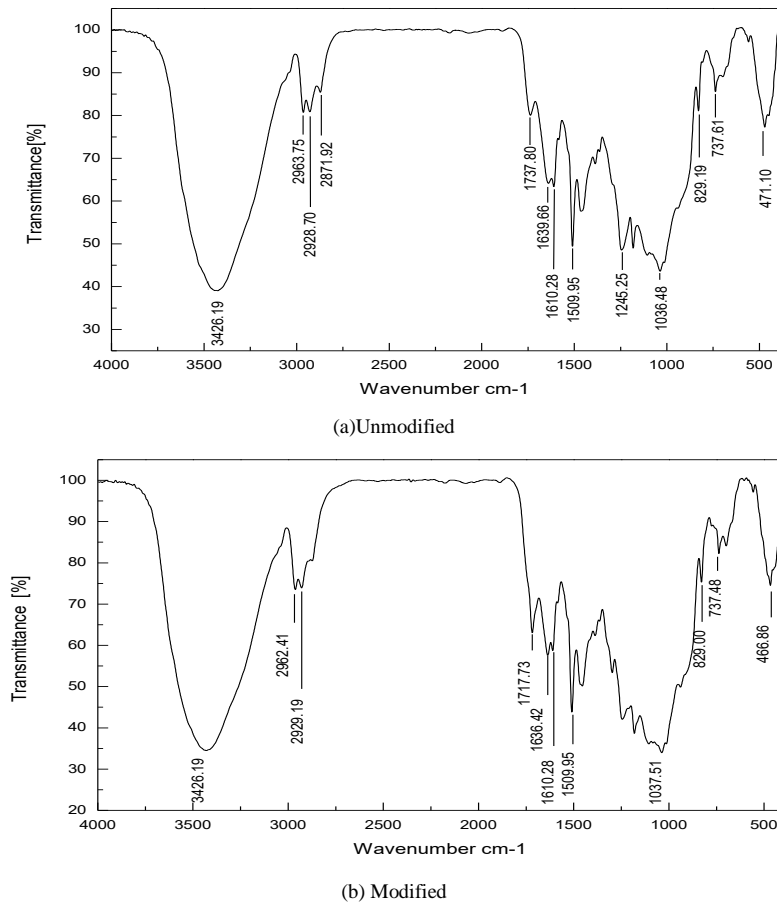


Fig. 4. IR spectrum of AP

Fig. 4 shows the infrared spectroscopy (IR) analysis of the AP with and without modification. Due to the existence of thermosetting resin, it's found a C-H bond absorption peak between 2972cm^{-1} and 2926cm^{-1} as well as a C=O bond absorption peak near 1735cm^{-1} in the unmodified AP.

After the modification by KH570 and styrene, the absorption peak between 2972cm^{-1} and 2926cm^{-1} is obviously enhanced, consistent with the stretching vibration band of the C-H bond of the modification agent. Meanwhile, the absorption peak near 1735cm^{-1} is also enhanced, consistent with the vibration peak of the C=O bond of the modification agent. Therefore, the surface modification has taken effect through low dose of modification agent by grafting on the SRCCL.

5. Conclusions

- 1 The SRCCL is mainly composed of resin (39% ~ 41%), glass fiber and mineral wool (56%~58%). According to the micro-shape analysis, most of the glass fiber has relatively complete surface with the size ranging from $20\mu\text{m}$ to $100\mu\text{m}$ and the others are agglomerates, which are some small size glass fiber not being completely shattered and surrounded by resin with the size of $10\mu\text{m}$.

- 2 The AP prepared by 70% modified SRCCL not only reduces the dosage of the adhesive, but also manifests a better physical properties than unmodified one, with a flexure strength over 25MPa and a lower water absorption. The surface modification has taken effect through low dose of modification agent by grafting on the SRCCL.
- 3 The AP is produced by a self-developed mechanical former. This technique offers a possibility for recycling of SRCCL and resolving the environmental pollutions during recycling of PCBs.

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